Abstract

The goal of molecular spintronics is to use molecules for the realization of smallest switchable magnetic units. The molecules serve as building blocks of future electronic devices to increase their integration density and energy efficiency. The interaction of individual molecules and molecular monolayers with metal surfaces is one of the key properties and needs to be investigated and controlled. To this end, well-defined and controlled adsorption of molecules with sub-monolayer coverage onto clean single-crystalline surfaces of (transition) metals under ultra-high vacuum conditions is required. In this PhD thesis, the chemisorption of three aromatic molecules on different transition metal surfaces and the associated formation of molecular hybrid magnets was investigated. This research was inspired by the experimental evidence of a molecule-based spin filter effect in mesoscopic junctions given by Raman et al. This thesis focuses on the basics with regard to the experimental realization of the spin-filter effect in a single double-decker molecule. The theoretically proposed spin-filter mechanism is based on the adsorption of intrinsically non-magnetic flat aromatic molecules on ferromagnetic surfaces, whereby strong hybridization of molecular π-orbitals with spin-split d-orbitals of the substrate occurs. The resulting imbalance of spin-resolved states of the adsorbed molecule induces magnetic properties in the molecule such as a spin-dependent band gap, a stable magnetic moment, or spin polarization at the Fermi energy. The induced magnetic properties as well as the atomic and electronic structure of the molecule-substrate hybrid systems are investigated by (spin-polarized) scanning tunneling microscopy and spectroscopy in ultra-high vacuum and at low temperatures (4 K).

First, preliminary studies on the adsorption of the flat aromatic molecules pyrene and HBC on Au(111) or Fe/W(110) and on Co/Cu(111), respectively, were carried out, since both molecules were considered at the beginning of the project as essential aromatic building blocks of specially designed double-decker molecules. Suitable double-decker molecules must be designed in such a way that the π-systems of two aromatic building blocks are densely stacked at a smaller distance than the van der Waals distance, which leads to a direct intramolecular π-π interaction. The Fc-Py^2-Fc double-decker molecule, which was finally successfully synthesized in Prof. Kögerler's research group, fulfils all primary requirements as a possible molecular spin filter. It is characterized by two bridged pyrene (Py) molecules stacked on top of each other and fixed by two ferrocenes (Fc). The Fc-Py^2-Fc molecule was successfully deposited on ferromagnetic Co nanoislands on Cu(111) and investigated in detail. The comparison of the properties of the Fc-Py^2-Fc molecules and their appearance on Co(111) and Cu(111) surfaces shows striking differences from which chemisorption on the Co surface can be derived. Spin-polarized measurements confirm this observation and show the formation of a molecular hybrid

magnet with spin polarization inverted relative to the substrate at the ferrocene positions, while no significant spin polarization could be measured at the pyrene position. On the one hand, this result can be explained by a strong energy and intramolecular position dependence of spin polarization. On the other hand, a hitherto undiscussed hybridization effect is proposed in which the strong interaction of the lower π-system with the Co-surface leads to a displacement of the π-orbital towards the substrate, which increases the effective distance between the two π-systems in the molecule. The reduced intramolecular π-π interaction in the chemisorbed Fc-Py$^{\mathbf{2}}$-Fc molecule could also explain the strongly suppressed spin polarization at the pyrene position.